ISSN 0128-0740
BULETIN FKKKSA 8(1) : 43 , 1994

THE EFFECT OF ADDITION OF LDPE ON THE MELTING AND CRYSTALLIZATION CHARACTERISTICS OF PIGMENTED PP

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ABSTRACT

Blends of PP pigmented with red iron oxide and LDPE were prepared by melt mixing in an injection molder. The thermal characteristics of the blends were analyzed using DSC. The blends were completely immiscible as shown by the presence of two distinct melting and crystallization peaks. The melting point of PP decreased with increasing content of PE whereas that of PE was not much affected. The crystallization transitions of PP (T_{onset} and T_C) shifted toward higher temperatures which showed that both PE and iron oxide acted as nucleating sites for PP. The overall crystallinity of both PP and PE decreased with increasing content of the other polyolefin component. Such effect was due to the kinetic and thermodynamic effects as well as to different rates of crystallization.

INTRODUCTION

Progress in science and technology has led to a growing demand for specialty plastics and more complex systems. However, new resins are not always required to meet needs for new materials. Development of a new polymer from concept to pilot scale can take 10 to 15 years at a cost of 10 to 50 million dollars with no guarantee of commercial success.[1] Construction of the actual plant requires another huge capital. For these reasons, the simplicity of blending is economically more appealing than the development of new chemistry.

Blending enables combination and modification of properties of the components, which may lead to some synergism as well as cost reduction of the expensive resins. Since the properties of existing blends are functions of compositions, a blend can be easily modified to meet performance and cost objectives required by new or changing markets. Recycling of plastics waste by blending is of environmental and commercial importance. The combination of polyethylene and polypropylene is particularly important because these two polymers are consumed in large volumes and therefore constitute a significant portion of plastic waste and scraps. Secondly, they are difficult to separate from each other in waste recovery operations.

The objective of this work is to investigate both the melting and crystallization characteristics of blends of low density polyethylene (LDPE) with polypropylene (PP) containing red iron oxide pigment particles.

LITERATURE REVIEW

It is known that most substances (and as such, neat resins) tend to crystallize pure. The additives are normally rejected from the growing crystal. For semi-crystalline polymer blends, this frequently means that, independently of miscibility in the molten state, there is

phase separation at crystallization temperatures.[2] The crystallization behavior of immiscible blends is therefore equivalent to that of the neat constituents, i.e. it takes place within a domain of nearly pure polymer.[2]

Crystallization from the melt occurs when the system is cooled below its melting temperature (T_m) to the crystallization temperature (T_c). The difference (T_m - T_c) is a measure of supercooling, which depends on the cooling rate and nucleation mechanism. In blends, a decrease in the degree of supercooling indicates an increase in the crystallization rate.[3] In the preparation of thermoplastic blends, the important nucleation mechanisms are (1) orientation induced nucleation caused by alignment of macromolecules and spontaneous crystallization; and (2) heterogeneous nucleation on the surface of foreign phases or particles.[2]

The heterogeneous nucleation brought about by a small amount of PE was found to increase the crystallinity of PP.[3-5] By contrast, another work[6] reported that the addition of LDPE brought about a negative effect on the primary nucleation of PP and depressed its overall rate of crystallization. The depression in the equilibrium melting point (T_m) of PP in the PP/LDPE blends was due to kinetic and morphological effects. Haghighat[5] explained the depression of the PP melting point in the PP/LLDPE blends in terms of the Flory theory of melting point depression of polymer-diluent mixture.

Gupta et. al[4] have used DSC to investigate how the presence of HDPE and glass fibers in the PP matrix might affect the latter's crystallization characteristics. Their exotherm data showed that the presence of small amounts of HDPE in PP resulted in enhancement of the rate of nucleation of PP, narrower PP crystallite size distribution and an increase in PP crystallinity not only in PP/HDPE blends, but also in PP/glass fiber/HDPE composites. The effects were found to be more pronounced in the presence of glass fibers, suggesting that the number of sites on which crystallization could occur had increased. The constraint imposed by the crystallized PP domains impeded the crystallization of the HDPE phase.

EXPERIMENTAL

Materials

The neat polyolefins used for this study, homopolypropylene NESTE VA4020E (MFI 0.4, ρ = 0.901g/cm^3, M_w/M_n = 5.67) and low density polyethylene NESTE NCPE 2224 (MFI 20, ρ = 0.924 g/cm^3, M_w/M_n = 30.6) were purchased from NESTE Belgium. The characteristics of the pigment used are indicated in Table 1.

Preparation of PP 'Masterbatch'

Several masterbatch compounds were prepared. PP and Fe_2O_3 pigment were weighed accordingly to contain 0.5% by weight pigment, and mechanically mixed prior to compounding by twin-screw extrusion. The extrudates were pelletized and vacuum dried. The pigment content was ascertained via gravimetric ashing.

Table 1b Physical and chemical characteristics of micronized Bayferrox 110M iron oxide.

Predominant particle size, mm	0.09
Density,g/cm^3	5.00
Color	Red
Particle shape	Spherical
Nature of pigment	Inorganic
Loss on heating at 1000°C in 1/2h, %	0.002
Chemical composition,%:	
Fe_2O_3	94-96
$SiO_2 + Al_2O_3$	2 - 4
Water-soluble salts	0.5

Blending and Sample Preparation

Mixing and preparation of the blends were accomplished by screw injection molding. Since the densities of the two polymers were similar, weight percent was used as an approximation to volume percent. Pellets of PP-masterbatch (PP) and LDPE were blended to PP/PE compositions of 100/0, 80/20, 65/35, 50/50, 35/65, 20/80 and 0/100 and molded into tensile specimens (ASTM D638 Type I) and notched Izod bars (ASTM D256) (reserved for subsequent work). The runners were granulated for thermal studies.

Thermal Analysis

Thermal characterization was carried out using a differential scanning calorimeter (DSC) Du Pont 2000. Approximately 10-11mg samples were heated from room temperature to 200°C in nitrogen at 10°C/min to determine the melting temperatures (T_m) and heats of fusion (DH_f). Samples were held at that temperature for 2 min, followed by cooling to room temperature at 10°C/min to record the crystallization data. Cooling was accomplished by liquid nitrogen. Al sample pans were used for all analyses.The crystallinity of each phase in the blend was calculated according to equation :

$$\%\text{crystallinity} = \frac{\Delta H_{sample}}{\Delta H_{100\%}} \times 100\%$$

where DH_{sample} is the area under curve in the thermogram in J/g, and $DH_{100\%}$ is the heat of fusion of theoretically 100% crystalline polymer. For PE and PP, $DH_{100\%}$ = 68.5 cal/g and $DH_{100\%}$ = 50 cal/g, were used respectively.[7] (For conversion to J/g, multiply by 4.184).

RESULT AND DISCUSSION

Table 2 summarizes the data obtained from the DSC fusion and crystallization thermograms. The results will be analyzed in terms of the following quantities:

1) the peak temperatures in the melting endotherms (T_m) and crystallization exotherms (T_c) of both PP (including neat resin) and LDPE,

2) the temperature at the onset of PP crystallization, i.e., the temperature where the curve initially departed from the baseline (T_{onset}),
3) the width of crystallization peak as calculated by the difference between T_{onset} and T_c. The values provided some indication on the crystallite size distribution.
4) the area under the curve (J/g) for PP and LDPE in both the endotherm and exotherm. These are proportional to the heat of crystallization and hence, the degree of crystallinity.

All the thermograms (refer to Table 2a and also Fig. 1) of the blends showed two distinct melting and crystallization peaks relative to the PP-masterbatch and LDPE, which crystallized separately, i.e. no co-crystallization occurred in the blends. The DSC traces of blends showed that the melting peaks of the two components were not modified by blending. This indicated the complete immiscibility of the two crystalline phases.

The higher peak temperatures were attributed to the PP phase while the lower ones corresponded to LDPE phase. Table 2a showed that the T_m of the PP-masterbatch in the blends were lower than that of 100% PP-masterbatch and decreased with increasing LDPE content. Both the T_m and T_c of LDPE phase in the blends showed very small variation from its pure resin with values centering around 113°C and 95-96°C, respectively. The melting point depression of the PP component in the blends was probably due to one of the following effects:-

1) the kinetic effect of one solid phase which might obstruct or make irregular the growth of the lamellar crystallites of the other phase; 6
2) thermal perturbations due to different rates of crystallization between PE and PP;
3) the thermodynamic effect exerted by LDPE which acted like a diluent in the system.[4,5]

In the crystallization exotherms, the T_c of the PP-masterbatch shifted towards a higher temperature compared to that of pure PP homopolymer. This suggested that iron oxide particles might promote heterogeneous nucleation in the masterbatch. Table 2a showed that, in general, PP-masterbatch crystallization commenced at even a higher temperature in the presence of LDPE as evidenced by T_{onset} and T_c for all blends. It could be that both the iron oxide and the PE acted as nucleation sites in the blends and promoted early onset of crystallization of PP.

When the melting peak and crystallization peak for each sample were compared, it can be seen that the peak width was narrower during the crystallization cycle. The difference was probably due to the different thermal crystallization history between the first cooling cycle (in the cold mold) and the second cycle (controlled cooling in the DSC cell). It should be pointed out that all blends were processed at 210°C in the injection molding machine. Therefore, even though the samples were held isothermally at 200°C for 2 min to minimize the effect of the previous thermal history, it might be possible that the previous processing history was not completely destroyed. The broad melting peak indicated that the samples cooled during the injection molding process melted over a broader temperature range. This implied that rapid cooling in the cold mold produced a broad distribution of crystallite size which might also include small and/or imperfect entities.

Crystallinity, as represented by the area under the exotherm curve, broadly showed a decrease for PP as well as PE with an increasing content of the other component. (See Table 2b) The decrease in PE crystallinity could be attributed to the fact that, in the blends, PP-masterbatch domains which crystallized first were likely to impose some

constraints on the LDPE phase (i.e. Effect 1) and consequently, the crystallization of PE was hindered.[6] The thermodynamic effect[4,5] (i.e. Effect 3) brought about by LDPE (lower M_n), which acted as a diluent, probably caused the decrease in crystallinity of PP in the blends. At both ends (i.e 80PP/20PE and 20PP/80PE), crystallinity of the minor components were largely hindered. Although it was mentioned earlier that LDPE possibly promoted heterogeneous nucleating sites which caused PP crystallization to commence early, this did not necessarily imply an increase crystallite perfection because the melting point of PP was lowered.

CONCLUSION

DSC analysis shows no co-crystallization takes place in the blends. The pigment particles promote heterogeneous nucleation in the PP. The decrease in crystallinity of the PE phase and PP phase with increasing content of the other phase is due to the kinetic and thermodynamic effect, respectively. No filler rejection phenomenon takes place in the blends as implied by DSC data on crystallinity of the LDPE phase.

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Table 2a Melting, crystallization and onset of crystallization temperature of PP-masterbatch/LDPE blends: DSC data

Blend System PP/LDPE	Melting Temp T_m°C		Crystallization Temp T_c°C		Onset of Cryst. of PP phase T_{onset}
	PP	LDPE	PP	LDPE	
Neat PP	166.08	-	110.39	-	116.64
100PP	166.31	-	113.98	-	118.89
80PP	165.97	113	114.14	96.22	120.47
65PP	166.09	113.13	116.07	96.38	125.45
50PP	165.43	113.08	117.00	95.85	122.92
35PP	164.47	113.17	115.09	95.70	121.37
20PP	163.76	113.21	113.11	95.96	118.27
0PP	-	113.33	-	94.75	-

Table 2b Percent crystallinity of PP-masterbatch and LDPE calculated from fusion endotherm and crystallization exotherm: DSC data

Blend System PP/LDPE	Heat of fusion ΔH_f (J/g)		% crystallinity after inj. moulding		Heat of crstallization ΔH_c (J/g)		% crystallinity after recrystallization in DSC cell	
	iPP	LDPE	iPP	LDPE	iPP	LDPE	iPP	LDPE
Neat PP	65.08	-	31.14	-	80.26	-	38.40	-
100/0	72.96	-	34.91	-	88.10	-	42.15	-
80/20	59.55	11.79	28.49	4.11	64.64	7.70	30.93	2.69
65/35	53.34	32.87	25.52	11.46	54.67	24.80	26.16	8.65
50/50	35.69	55.18	17.08	19.24	36.52	55.48	17.47	19.35
35/65	27.14	66.25	12.99	23.10	29.23	60.41	14.03	21.07
20/80	9.77	70.41	4.67	24.56	7.91	69.17	3.78	24.12
0/100	-	85.48	-	29.81	-	85.58	-	29.85

ISSN 0128-0740
BULETIN FKKKSA 8(1) : 49 , 1994

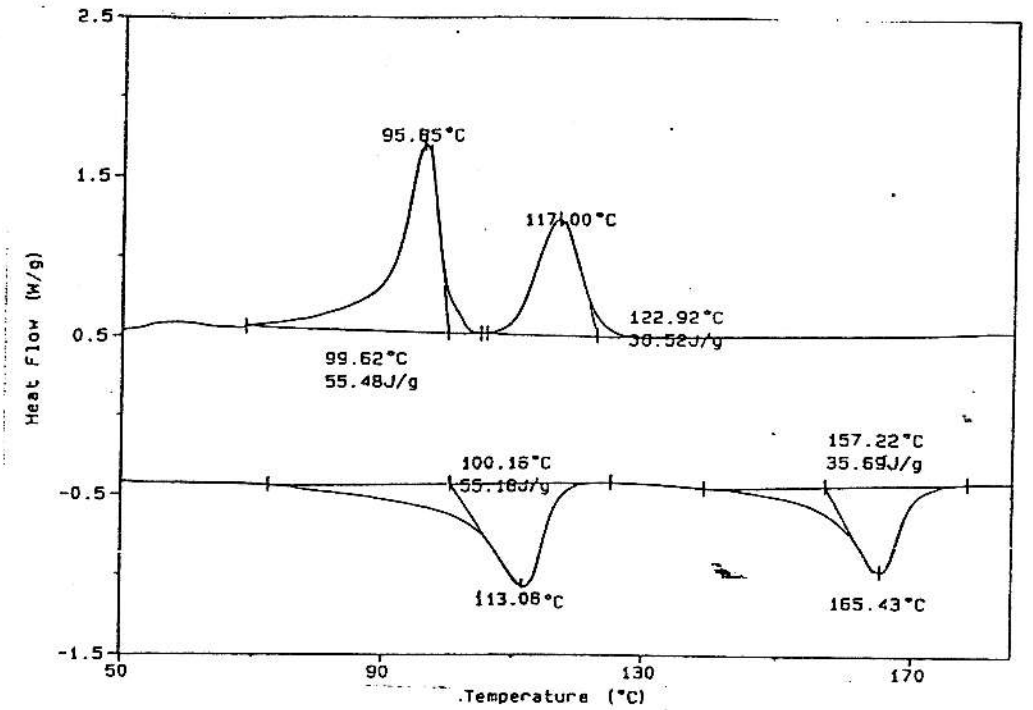

Fig. 1 DSC thermogram for blend containing 50% LDPE. The lower trace is recorded during the heating cycle, the upper one during cooling.